An experimental study of the effect of mineral dissolution reactions on the reactive surface area and permeability of sandstone

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The coupling of fluid flow and fluid-mineral interaction is essential to understand the modification of porous rocks physical properties in natural environments. For example, in sedimentary basins, rocks experience a complex series of diagenetic processes including mineral/cement dissolution and precipitation, compaction, and recrystallization. All these processes are strongly influenced by fluid flow (Bjørlykke et al., 1989; Lasaga and Rye, 1993). For this reason, knowledge of the evolution of permeability, reactive surface area, and porosity in the presence of a percolating fluid is necessary for the development and validation of theoretical reaction-transport models. Unfortunately, the temporal dependence of these parameters has never been investigated in detail which force most of the present models to assume constant reactive surface areas or to estimate them using simple geometrical equations. Such assumptions are inconsistent with data obtained from natural weathering systems that indicate a dramatic increase of surface area with time (White, 1995).

Experimental methodology

Experiments were conducted on Fontainebleau sandstone cores (~100% quartz) from the Ile de France region. The core dimensions are 2.2 cm in diameter and 4.5 cm long. The percolation cell is composed of an externally-heated single-pass flow-through reactor fitted with a pressure transducer to measure differential pressures and thus permeabilities according to Darcy's law at continuous fluid flow velocities of 1–14,000 m/yr. The sandstone core is enclosed within a rubber jacket at a constant confining pressure of ~6 bar to avoid fluid percolation around the sample. The input solution was prepared from a 1 Molar reagent-grade NaOH solution diluted in double-distilled water to produce a 0.1 Molar NaOH concentration and pH 13 at 25°C.

The reason for using an alkaline input solution is to increase quartz dissolution rates and induce significant changes in the rock flow properties in a relatively short period of time. Fluid samples were taken daily for $SiO_2(aq)$ concentration and pH analyses. In situ permeability measurements were taken at 25°C during the initial stage of percolation and at 80°C for the remaining time of the experiment. Solution viscosity was corrected at both temperatures for determination of permeability. During heating, the core permeability decreased significantly (by a factor of ~4). This permeability decrease with increasing temperature is probably due to the thermal expansion of quartz.

Experimental results and discussion

The reactive surface area is computed from measured outlet fluid composition using,

$$\bar{A}_r = \frac{C_{SiO_2(aq)}q}{K_{diss}V_{core}} \qquad (1)$$

where $\bar{A}_r$ is the estimated reactive surface area (cm^{-1}), $C_{SiO_2(aq)}$ is the outlet $SiO_2(aq)$ concentration (moles/L), q is the volumetric flow rate (L/s), K_{diss} is the experimentally determined quartz dissolution rate constant (moles/cm^2 s) normalized to BET surface areas, and V_{core} refers to the core volume (cm^3). k_{diss} used in this calculation was obtained from Dove (1994) and equals 5.00×10^{-13} moles/cm^2 s. The temporal variation of reactive surface area of a core having an original total porosity of 8.9% and a permeability of 26.8 mD at 25°C is shown in Fig. 1. The increase in reactive surface area apparent in this figure results from a corresponding increase in $C_{SiO_2(aq)}$. The reactive surface area increased from 128 to 427 cm^{-1}, an increase of a factor of ~3.3 during this experiment which lasted 52 days. This large temporal increase in reactive surface area is due to pervasive mineral dissolution caused by the
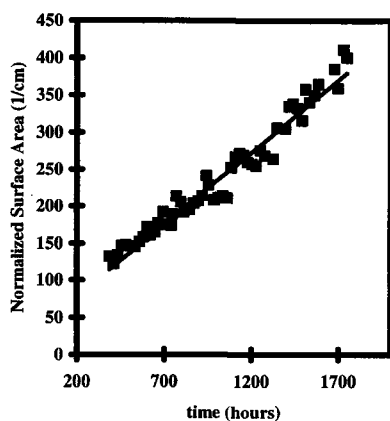
FIG. 1. Normalized reactive surface area (cm^{-1}) vs elapsed time. Filled squares are experimental data, solid line is a linear fit through the data.
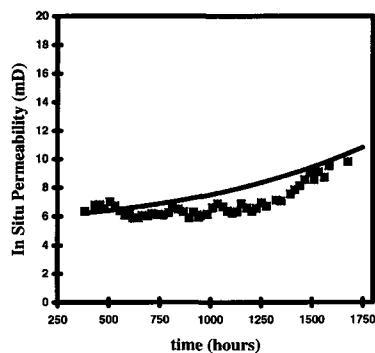

FIG. 2. *In situ* permeability (solid squares) vs elapsed time. The solid line corresponds to $k \propto \phi^{3.8}$ as suggested by Doyen (1988) for the Fontainebleau sandstone (see text).

introduction of the reactive percolating fluid. The initial reactive surface area is similar to that predicted by geometric models. For example, the intergrown sphere model of Canals and Meunier (1995) suggests a reactive surface area 100.3 cm^{-1} for this sandstone. It seems likely that the increase in reactive surface area with time reflects the enhanced roughening of quartz surfaces due to the formation of dissolution textures such as etch pits. This dramatic increase in reactive surface area with mineral dissolution during this experiment is in good qualitative agreement with observations of natural systems (White, 1995).

In situ permeability measurements during this experiment are shown in Fig. 2. The permeability in the first ~1342 hours (52 days) remained at a relatively constant value of 6.5 ± 0.2. After this time period, permeability increased slowly with time to approximate 1.3 times of its original value. This suggest that dissolution during this first stage involves a process of mineral surface roughening along with possible fine particle dissolution within the pore structure prior to a subsequent enlargement of connecting pore-throats and channels that can consequently increase permeability. This permeability evolution coincides with an increase in the core porosity from 8.9 to 10.3% due to quartz dissolution. The solid curve on Fig. 2 is consistent with a proportionality between the permeability and $\phi^{3.8}$ (see Doyen, 1988), similar to a traditional cubic law ($k \propto \phi^3$. This curve was generated by normalizing the calculation to the first data point. The qualitative correspondance between the curve and the data points in Fig. 2 indicates that this traditional proportionality is roughly consistent

with experimental results.

The experimental results obtained in this study indicate that the major effect of mineral dissolution reactions is on the reactive surface area rather than on the permeability or porosity. This conclusion has major consequences for mass transport calculations in weathering environments. Due to the enhancing effect of dissolution reactions on reactive surfaces areas, chemical weathering and diagenesis is a self-accelerating process. These effects are particularly significant for natural open systems where large mass transfer fluxes are common and enhancement of reactive surface areas can greatly increase weathering rates. It is envisioned that these results will be used to develop quantitative formulations describing the evolution of reactive surface area as a function of reaction progress in a dynamic geochemical systems. These formulations can be incorporated into reaction-transport models to predict more accurately the temporal evolution of water-rock properties over geologic time frames.

References

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